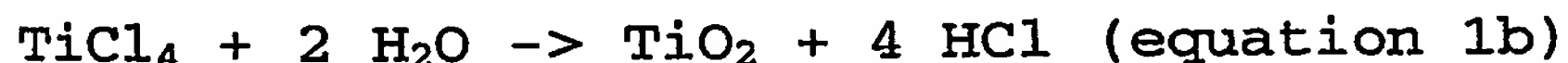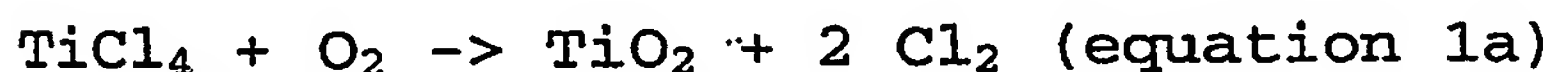# Flame-hydrolytically Produced Titanium Dioxide Powder

The invention relates to flame-hydrolytically produced
titanium dioxide powder, and its production and use.

5

It is known that titanium dioxide can be produced by
pyrogenic processes. Pyrogenic processes are understood to
include flame oxidations or flame hydrolyses. In flame
oxidation a titanium dioxide precursor, for example
10 titanium tetrachloride, is oxidised with oxygen according
to equation 1a. In flame hydrolysis the formation of
titanium dioxide is effected by hydrolysis of the titanium
dioxide precursor, the water necessary for the hydrolysis
being derived from the combustion of a fuel gas, for
15 example hydrogen, and oxygen (equation 1b).


$$TiCl_4 + O_2 \rightarrow TiO_2 + 2\ Cl_2 \quad \text{(equation 1a)}$$

$$TiCl_4 + 2\ H_2O \rightarrow TiO_2 + 4\ HCl \quad \text{(equation 1b)}$$

20
EP-A-1231186 claims a titanium dioxide with a BET surface
of between 3 and 200 $m^2/g$ with a weight-related $D_{90}$ diameter
of the particles of 2.2 µm or less. $D_{90}$ diameters of between
0.8 and 2.1 µm are mentioned in the examples of
25 implementation. In addition, a titanium dioxide is
obtained with a BET surface of between 3 and 200 $m^2/g$ and a
distribution constant n of 1.7 or more, calculated
according to the formula $R = 100\ \exp(-bD^n)$, where D denotes
the particle diameter and b is a constant. The value n is
30 obtained from the three values $D_{10}$, $D_{50}$ and $D_{90}$, which are
related to one another by an approximate straight line.
The titanium dioxide is obtained by a flame oxidation of
titanium tetrachloride and an oxidising gas, the starting

materials being pre-heated to a temperature of at least
500°C before the reaction.  In preferred embodiments the
velocity of the reaction mixture is 10 m/sec or more, and
the residence time in the reaction space is 3 sec or less.

5

In EP-A-778812 a process for the production of titanium
dioxide by a combination of flame oxidation and flame
hydrolysis is described.  In this connection titanium
tetrachloride in the vapour state and oxygen are mixed in a
10    reaction zone and the mixture is heated in a flame that is
generated by combustion of a hydrocarbon as fuel gas.  The
titanium tetrachloride is fed into the central core of the
reactor, the oxygen is fed into a tubular sleeve
surrounding the central core, and the fuel gas is fed into
15    a tubular sleeve that surrounds those tubes that convey the
titanium tetrachloride and oxygen.

A laminar diffusion flame reactor is preferably employed.
In this method it is possible to produce highly surface-
active titanium dioxide powder containing a large
20    proportion of the anatase modification.  In EP-A-778812 no
information is given regarding the structure and size of
the primary particles and aggregates.  However, it is these
quantities in particular that are important for many
applications, for example in cosmetics applications or as
25    an abrasive in dispersions for the electronics industry.
The mechanism of the formation of the titanium dioxide
according to EP-A-778812 includes both a flame oxidation
(equation 1a) as well as a flame hydrolysis (equation 1b).
30    Although the different formation mechanisms enable the
anatase fraction to be controlled, a specific distribution
of the primary particles and aggregates cannot however be
achieved.  A further disadvantage of this method, as is

mentioned in US-A-20002/0004029, is the incomplete
conversion of titanium tetrachloride and fuel gas and the
resultant grey colouration of the titanium dioxide.

5    These problems are eliminated according to US-A-
20002/0004029, by now using five tubes instead of the three
tubes as described in EP-A-778812. For this, titanium
tetrachloride vapour, argon, oxygen, hydrogen and air are
simultaneously metered into a flame reactor. The
10   disadvantage of this method is the use of the expensive
noble gas argon and a low yield of titanium dioxide due to
low concentrations of titanium tetrachloride in the
reaction gas.

15   A titanium dioxide powder produced by flame hydrolysis has
for a long time been marketed by Degussa under the
reference P 25.

This is a finely particulate titanium dioxide powder with a
20   specific surface of $50\pm15$ m$^2$/g, a mean size of the primary
particles of 21 nm, a compacted bulk density (approximate
value) of 130 g/l, an HCl content of less than or equal to
0.300 wt.% and a screening residue according to Mocker
(45 µm) of less than or equal to 0.050%. This powder has
25   good properties for many applications.

The prior art demonstrates the wide interest in
pyrogenically produced titanium dioxide. In this
connection it is found that the common generic term
30   "pyrogenic", i.e. flame hydrolysis and flame oxidation, is
not an adequate description of titanium dioxide. On
account of the complexity of the pyrogenic processes only a
few substance parameters can be specifically adjusted.

Titanium dioxide is employed in particular in catalysis,
for example photocatalysis, in cosmetics, for example
sunscreen agents, as an abrasive in the form of dispersions
in the electronics industry, or for heat stabilisation of

5    polymers.   In these uses increasing demands are placed on
the purity and structure of the titanium dioxide.   Thus, it
is for example important that, when using titanium dioxide
as an abrasive in dispersions, the titanium dioxide has a
good dispersibility and is as far as possible free from

10   coarse particles that can scratch the surface to be
polished.

The object of the present invention is to provide a
titanium dioxide powder that has a high purity, is easy to

15   disperse, and is as far as possible free of coarse
fractions.

The object of the present invention is also to provide a
process for the production of the titanium dioxide powder.

20   In this connection the process should be able to be
implemented on an industrial scale.

The present invention provides a flame-hydrolytically
produced titanium dioxide powder that is present in

25   aggregates of primary particles, characterised in that

-    it has a BET surface of 20 to 200 $m^2/g$ and

-    the half width HW, in nanometers, of the primary

30        particle distribution has values between

HW [nm] = a x BET$^f$ where a = $670 \times 10^{-9}$ m$^3$/g and

$-1.3 \leq f \leq -1.0$ and

-       the proportion of particles with a diameter of more
5       than 45 µm is in a range from 0.0001 to 0.05 wt.%.

The term primary particles in the context of the invention
is understood to denote particles that are first of all
formed in the reaction and that can coalesce to form
10   aggregates during the further course of the reaction.

The term aggregate within the context of the invention is
understood to denote primary particles of similar structure
and size that have coalesced together, and whose surface is
15   smaller than the sum of the individual, isolated primary
particles. Several aggregates or also individual primary
particles may combine together further to form
agglomerates. Aggregates or primary particles accordingly
lie adjacent to one another in the form of point objects.
20   Depending on their degree of coalescence, agglomerates may
be broken up by application of energy.

Aggregates on the other hand can be broken up only by a
high input of energy or even cannot be broken up at all.
25   Intermediate forms exist.

The mean half width HW of the primary particle distribution
(in numerical terms) is obtained by image analysis of the
TEM photographs. According to the invention the mean half
30   width is a function of the BET surface with a constant f,
where $-1.3 \leq f \leq -1.0$. Preferably the half width may lie
in the range $-1.2 \leq f \leq -1.1$.

It is the high BET surface, the narrow distribution of the
primary particle distribution and the low proportion of
aggregates with a diameter of more than 45 µm, which lies
5    in a range from 0.0001 to 0.05 wt.%, that are relevant for
the positive properties of the powder according to the
invention, for example when polishing surfaces.  No flame-
hydrolytically produced titanium dioxide powders are known
in the prior art that simultaneously exhibit these
10   features.  It is of course possible for example to remove
to a large extent powders according to the prior art
mechanically from aggregates with a diameter of more than
45 µm, though the resultant powder would however not be
able to achieve the ranges claimed by the present invention
15   as regards BET surface and half width values of the primary
particles.

The BET surface of the titanium dioxide powder according to
the invention lies in a wide range from 20 to 200 $m^2/g$.  It
20   has proved advantageous if the BET surface lies in a range
from 40 to 60 $m^2/g$.  A range of 45 to 55 $m^2/g$ may be
particularly advantageous.

For a titanium dioxide powder according to the invention
25   with a BET surface between 40 and 60 $m^2/g$, the 90% spread of
the number distribution of the primary particle diameters
may lie between 10 and 100 nm.  As a rule the 90% spread of
the number distribution of the primary particle diameters
is between 10 and 40 nm.
30
Furthermore, the equivalent circular diameter of the
aggregates (ECD) of such a titanium dioxide powder may be
less than 80 nm.

The mean aggregate area of a titanium dioxide powder
according to the invention with a BET surface of 40 to
60 $m^2$/g may be less than 6500 $nm^2$ and the mean aggregate
circumference may be less than 450 nm.

5

In addition the BET surface of the titanium dioxide powder
according to the invention may lie in a range from 80 to
120 $m^2$/g.  A range of 85 to 95 $m^2$/g may be particularly
preferred.

10

For a titanium dioxide powder according to the invention
with a BET surface between 80 and 120 $m^2$/g, a 90% spread of
the number distribution of the primary particle diameters
may have values between 4 and 25 nm.  Furthermore, such a
15   titanium dioxide powder may have an equivalent circular
diameter of the aggregates (ECD) of less than 70 nm.

The mean aggregate area of a titanium dioxide powder
according to the invention with a BET surface of 80 to
20   120 $m^2$/g may be less than 6000 $nm^2$ and the mean aggregate
circumference may be less than 400 nm.

The proportion of aggregates and/or agglomerates of the
titanium dioxide powder according to the invention with a
25   diameter of more than 45 µm lies in a range from 0.0001 to
0.05 wt.%.  A range from 0.001 to 0.01 wt.% may be
preferred, and a range from 0.002 to 0.005 wt.% may be
particularly preferred.

30   The titanium dioxide powder according to the invention
comprises rutile and anatase as crystal modifications.  In
this connection the anatase/rutile proportion for a given
surface may lie in a range from 2:98 to 98:2.  The range
from 80:20 to 95:5 may be particularly preferred.

35

The titanium dioxide powder according to the invention may
contain residues of chloride.  The chloride content is

8

preferably less than 0.1 wt.%. A titanium dioxide powder
according to the invention with a chloride content in the
range from 0.01 to 0.05 wt.% may be particularly preferred.

5   The compacted bulk density of the titanium dioxide powder
according to the invention is not limited. It has however
proved advantageous if the compacted bulk density has
values from 20 to 200 g/l. A compacted bulk density of 30
to 120 g/l may be particularly preferred.
10
The present invention also provides a process for the
production of the titanium dioxide powder according to the
invention, which is characterised in that

15  -   a titanium halide, preferably titanium tetrachloride,
        is vapourised at temperatures of less than 200°C, the
        vapours are transferred to a mixing chamber by means
        of a carrier gas with a proportion of steam in a range
        from 1 to 25 g/m$^3$, and
20
    -   separately from this, hydrogen, primary air, which may
        optionally be enriched with oxygen and/or pre-heated,
        and steam are transferred to the mixing chamber,

25      -   wherein the proportion of steam is in a range
            from 1 to 25 g/m$^3$ primary air,

        -   the lambda value lies in the range from 1 to 9
            and the gamma value lies in the range from 1
30          to 9,

        following which

    -   the mixture consisting of the titanium halide vapour,
35      hydrogen, air and steam is ignited in a burner and the
        flame burns back into a reaction chamber sealed from

the ambient air, wherein

- a vacuum of 1 to 200 mbar exists in the reaction chamber,

5

- the exit velocity of the reaction mixture from the mixing chamber to the reaction space lies in a range from 10 to 80 m/sec,

10   - in addition secondary air is introduced into the reaction chamber, wherein

- the ratio of primary air to secondary air is between 10 and 0.5,

15

- following which the solid is separated from gaseous substances, and

- the solid is then treated with steam.

20

An essential feature of the process according to the invention is that the titanium halide is vapourised at temperatures below 200°C and the vapours are conveyed to the mixing chamber by means of a carrier gas, for example

25   air or oxygen, which has a defined carrier gas moisture content.  It has been found for example that the product quality decreases at higher vapourisation temperatures.

Moreover it has also been found that, within the claimed

30   steam content of 1 to 25 g/m$^3$ of gas, or primary air, there is no noticeable hydrolysis of the titanium halide in the form of caking, whereas on the other hand the steam content influences the subsequent primary particle and aggregate structure.  Outside the claimed range, no powder according

35   to the invention can be obtained.  In a preferred embodiment the steam content is between 5 and 20 g/m$^3$ of gas, or primary air.

As carrier gas, air may also be used.  This permits a
higher space-time yield in the reaction chamber than when
using an inert gas.

5

Furthermore, the exit velocity of the reaction mixture from
the mixing chamber into the reaction space lies in a range
from 10 to 80 m/sec. In a preferred embodiment the exit
velocity is between 15 and 60 m/sec, and in a particularly
preferred embodiment is between 20 and 40 m/sec.  At values
below this a uniform powder is not obtained, but instead a
powder is obtained that contains particles of diameter
45 μm or more in an amount of more than 0.05 wt.%.

15    In addition the reaction must be carried out so that the
lambda value lies in the range from 1 to 9 and the gamma
value lies in the range from 1 to 9.

Flame-hydrolytically produced oxides are normally obtained
20    so that the gaseous starting substances are in a
stoichiometric ratio with respect to one another such that
the added hydrogen is at least sufficient to react with the
halogen X present from the titanium halide $TiX_4$ to form HX.
The amount of hydrogen required for this purpose is termed
25    the stoichiometric amount of hydrogen.

The ratio of the added hydrogen to the stoichiometrically
necessary hydrogen defined above is termed gamma.  Gamma is
defined as:

30

Gamma =    added hydrogen/stoichiometrically required
           hydrogen

or

35

Gamma =    $H_2$ fed in (moles)/$H_2$ stoichiometric (moles).

With flame-hydrolytically produced oxides in addition an
amount of oxygen (for example from the air) is normally
used that is at least sufficient to convert the titanium
halide into titanium dioxide and to convert excess hydrogen
5    that may still be present into water.  This amount of
oxygen is termed the stoichiometric amount of oxygen.

Similarly, the ratio of added oxygen to stoichiometrically
required oxygen is termed lambda, and is defined as
10   follows:

Lambda = added oxygen/stoichiometrically required oxygen

or

15

Lambda = $O_2$ fed in (moles)/$O_2$ stoichiometric (moles).

Moreover, in the process according to the invention, in
addition to the primary air in the mixing chamber air
20   (secondary air) is directly introduced into the reaction
chamber. It has been found that, without the addition of
the additional air into the mixing chamber, no titanium
dioxide powder according to the invention is obtained.  In
this connection it should be noted that the ratio of
25   primary air to secondary air is between 10 and 0.5.  The
ratio is preferably in a range between 5 and 1.

In order to be able accurately to meter in the amount of
secondary air, it is necessary to cause the flame to burn
30   back into a reaction chamber sealed from the ambient air.
This enables the process to be accurately controlled, which
is essential in order to obtain the titanium dioxide powder
according to the invention.  The vacuum in the reaction
chamber is preferably between 10 and 80 mbar.

35

An essential feature is also the fact that titanium dioxide
powder after separation from gaseous substances should be

treated with steam. This treatment is primarily intended
to remove halide-containing groups from the surface. At
the same time this treatment reduces the number of
agglomerates. The process may be carried out continuously
5   in such a way that the powder is treated, in counter-
current or co-current, with steam, possibly together with
air, in which connection the steam is always introduced
from below into an upright, heatable column. The feed of
the powder may take place from the top or the bottom of the
10  column. The reaction conditions may be chosen so that a
fluidised bed is formed. The temperature at which the
treatment with steam is carried out is preferably between
250 and 750°C, values from 450 to 550°C being preferred.
In addition it is preferred to carry out the treatment in
15  counter-current in such a way that a fluidised bed is not
formed.


Moreover it may be advantageous to introduce the steam
together with the air into the mixing chamber.
20
Fig. 1A shows diagrammatically an arrangement for carrying
out the process according to the invention. In the figure:
A = mixing chamber, B = flame, C = reaction chamber, D =
solid/gaseous separation, E = post-treatment with steam.
25  The substances used are identified as follows: a = mixture
of titanium halide and carrier gas with defined moisture
content, b = hydrogen, c = air, d = steam, e = secondary
air, f = steam or steam/air. Fig. 1B shows a section of
the arrangement of Fig. 1A. In this, the steam (d)
30  together with the air (c) are introduced into the mixing
chamber. Fig. 1C shows an open reaction chamber in which
the secondary air e is aspirated from the surroundings.
With the arrangement according to Fig. 1C no titanium
dioxide powder according to the invention can be obtained.

35

The invention also provides for the use of the titanium dioxide powder according to the invention for the heat protection stabilisation of silicones.

5    The invention in addition provides for the use of the titanium dioxide powder according to the invention in sunscreen agents.

The invention furthermore provides for the use of the
10   titanium dioxide powder according to the invention as a catalyst, as a catalyst carrier, as a photocatalyst, and as an abrasive for the production of dispersions.

**Examples**

<u>**Analysis**</u>

5    The BET surface is determined according to DIN 66131.

The compacted bulk density is determined on the basis of
DIN ISO 787/XI K 5101/18 (not screened).

10   The bulk density is determined according to DIN-ISO 787/XI.

The pH value is determined on the basis of DIN ISO 787/IX,
ASTM D 1280, JIS K 5101/24.

15   The proportion of particles larger than 45 µm is determined
according to DIN ISO 787/XVIII, JIS K 5101/20.

Determination of the chloride content: ca. 0.3 g of the
particles according to the invention is accurately weighed
20   out, 20 ml of 20 per cent sodium hydroxide solution
(analysis purity) are added thereto, dissolved, and
transferred while stirring to 15 ml of cooled $HNO_3$.  The
chloride content in the solution is titrated with $AgNO_3$
solution (0.1 mole/l or 0.01 mole/l).

25

The half width of the primary particle distribution and
area, circumference and diameter of the aggregates are
determined by means of image analysis.  The image analyses
are carried out using an H 7500 TEM instrument from Hitachi
30   and a MegaView II CCD camera from SIS.  The image
magnification for the evaluation is 30000 : 1 at a pixel
density of 3.2 nm.  The number of evaluated particles is
greater than 1000.  The preparation is carried out
according to ASTM3849-89.  The lower threshold boundary as
35   regards detection is 50 pixels.

## Example A1 (according to the invention)

160 kg/hr of $TiCl_4$ are vapourised in an evaporator at 140°C.
The vapours are transferred to a mixing chamber by means of
nitrogen (15 $Nm^3$/hr) as carrier gas with a carrier gas
moisture content of 15 g/$m^3$ of carrier gas.  Separately from
this, 52 $Nm^3$/hr of hydrogen and 525 $Nm^3$/hr of primary air
are introduced into the mixing chamber.  In a central tube
the reaction mixture is fed to a burner and ignited.  The
flame burns in a water-cooled flame tube.  In addition
200 $Nm^3$/hr of secondary air are added to the reaction space.
The powder formed is separated in a downstream filter and
then treated in countercurrent with air and steam at 520°C.

The **Examples A2 to A9 according to the invention** are
carried out similarly to A1.  The parameters altered in
each case are listed in Table 1.

The physicochemical data of the powders from Examples A1 to
A9 are shown in Table 2.

The **comparison examples B1 to B3 and B5 to B8** are also
carried out similarly to A1.  The parameters altered in
each case are listed in Table 1.

The **comparison example B4** is carried out using an open
burner.  The amount of secondary air is not determined.

The physicochemical data of the powders from Examples B1 to
B8 are shown in Table 2.

Table 3 shows the calculated half width of the primary
particles depending on the BET surface area with f=-1.0, -
1.05, -1.15 und -1.3. The factor $10^{-9}$ is the basis for the
conversion of meter into nanometer. As factor f can only be
negative, the unit of $BET^f$ is g/m2.

Fig. 2 shows the half width of the primary particles of the
titanium dioxide powders produced in the examples.  In this
connection the titanium dioxide powders according to the
5   invention (identified as ■) lie within the claimed half
width HW [nm] = a x $BET^f$ where a = $670 \times 10^{-9}$ $m^3$/g and
$-1.3 \leq f \leq -1.0$, while the comparison examples (identified
by +) lie outside.

**Table 1: Process parameters in the production of the titanium dioxide powders**

| Ex. | TiCl$_4$ | T$_V$ | Carrier Gas | Carrier Gas Moisture | H$_2$ | Primary Air | Primary Air Moisture | Secondary Air | Gamma | Lambda | v | T$_E$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | kg/h | | Nm$^3$/h | g/m$^3$ | Nm$^3$/h | Nm$^3$/h | g/m$^3$ | Nm$^3$/h | | | m/s | °C |
| A1 | 160 | 140 | 15 | 15 | 52 | 525 | 15 | 200 | 1.38 | 3.55 | 27 | 520 |
| A2 | 160 | 140 | 15 | 15 | 52 | 525 | 10 | 200 | 1.38 | 3.55 | 27 | 650 |
| A3 | 160 | 140 | 3 | 10 | 52 | 635 | 15 | 200 | 1.38 | 5.15 | 31 | 450 |
| A4 | 160 | 140 | 15 | 10 | 82 | 415 | 15 | 200 | 2.17 | 2.25 | 23 | 520 |
| A5 | 200 | 140 | 40 | 8 | 52 | 500 | 10 | 200 | 1.1 | 4.3 | 26 | 520 |
| A6 | 40 | 140 | 15 | 15 | 67 | 535 | 10 | 200 | 7.08 | 3.44 | 27 | 520 |
| A7 | 40 | 140 | 15 | 6 | 67 | 550 | 10 | 200 | 7.08 | 3.54 | 27 | 520 |
| A8 | 40 | 140 | 15 | 22 | 60 | 780 | 10 | 200 | 6.34 | 5.55 | 38 | 520 |
| A9 | 160 | 140 | 15 | 2 | 52 | 225 | 10 | 200 | 1.38 | 1.93 | 14 | 520 |
| B1 | 160 | 250 | 15 | 10 | 52 | 525 | 10 | 200 | 1.38 | 3.55 | 27 | 520 |
| B2 | 160 | 140 | 15 | 40 | 52 | 525 | 10 | 200 | 1.38 | 3.55 | 27 | 520 |
| B3 | 160 | 140 | 15 | 10 | 52 | 1200 | 12 | 200 | 1.37 | 9.67 | 56 | 520 |
| B4 | 160 | 140 | 15 | 10 | 52 | 525 | 12 | ** | 1.38 | 3.55 | 27 | 520 |
| B5 | 40 | 140 | 15 | 10 | 70 | 560 | 12 | 10 | 7.4 | 3.35 | 26 | 650 |
| B6 | 160 | 140 | 15 | 10 | 52 | 525 | 12 | 200 | 1.38 | 3.55 | 27 | - |
| B7 | 160 | 140 | 15 | 10 | 52 | 525 | 15 | 0 | 1.38 | 3.55 | 27 | 520 |
| B8 | 160 | 220 | 15 | 10 | 52 | 525 | 15 | 50 | 1.38 | 3.55 | 27 | 520 |

T$_V$ = temperature of evaporator; T$_E$ = deacidification temperature; B4: = open burner, no secondary air measurement; v = exit velocity of the reaction mixture from the mixing chamber into the reaction space

Table 2: Physicochemical parameters of the titanium dioxide powders

| Ex. | BET | Primary Particles Half Width | Aggregates ECD | Aggregates Avg. Area | Aggregates Avg. Circmf. | Particles > 45 µm | Anatase | Bulk Density | Compacted Bulk Density | Chlorine Content | pH-Value |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | m2/g | nm | nm | nm2 | nm | % | % | g/l | g/l | Wt.% |  |
| A1 | 48 | 11.0 | 67.4 | 4976 | 366.3 | 0.001 | 89 | 84 | 114 | 0.02 | 3.8 |
| A2 | 47 | 10.4 | 66.4 | 5112 | 369.5 | 0.001 | 89 | 88 | 115 | 0.15 | 4.2 |
| A3 | 49 | 9.3 | 65.3 | 4827 | 371.9 | 0.002 | 85 | 87 | 108 | 0.1 | 3.8 |
| A4 | 24 | 19.8 | n.d. | n.d. | n.d. | 0.003 | 52 | 96 | 114 | 0.05 | 4.0 |
| A5 | 43 | 13.5 | 66.5 | 5140 | 380.75 | 0.002 | 92 | 88 | 110 | 0.11 | 3.8 |
| A6 | 85 | 5.4 | 63.1 | 5017 | 341.0 | 0.010 | 93 | 102 | 122 | 0.15 | 3.9 |
| A7 | 91 | 4.8 | 62.4 | 5314 | 331.5 | 0.008 | 90 | 99 | 125 | 0.13 | 3.8 |
| A8 | 172 | 2.2 | 60.1 | 5128 | 321.0 | 0.009 | 96 | 115 | 158 | 0.09 | 3.7 |
| A9 | 49 | 34.3 | n.d. | n.d. | n.d. | 0.002 | 71 | 112 | 143 | 0.04 | 4.0 |
| B1 | 48 | 17.2 | 75.8 | 6525 | 448.3 | 0.019 | 89 | 83 | 106 | 0.03 | 3.8 |
| B2 | 49 | 16.0 | 81.2 | 6713 | 481.0 | 0.025 | 91 | 84 | 108 | 0.11 | 3.9 |
| B3 | 188 | 5.9 | 77.9 | 6418 | 452.3 | 0.004 | 97 | 111 | 162 | 0.09 | 4.0 |
| B4 | 48 | 16.6 | 82.3 | 7214 | 474.8 | 0.010 | 87 | 89 | 111 | 0.04 | 3.9 |
| B5 | 94 | 10.0 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| B6 | 51 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 1.51 | 2.3 |
| B7 | 49 | 18.4 | n.d. | n.d. | n.d. | 0.06 | 85 | n.d. | n.d. | 0.08 | 3.9 |
| B8 | 49 | 19.8 | n.d. | n.d. | n.d. | 0.11 | 87 | n.d. | 116 | 0.1 | 4.0 |

n.d. = not determined

## Tab. 3: Calculated half width of primary particles

| BET [m2/g] | Half width of primary particles [nm] | | | |
|---|---|---|---|---|
| | $670*10^{-9}*$ $BET^{-1,00}$ | $670*10^{-9}*$ $BET^{-1,05}$ | $670*10^{-9}*$ $BET^{-1,15}$ | $670*10^{-9}*$ $BET^{-1,3}$ |
| 20 | 33,50 | 28,84 | 21,37 | 13,64 |
| 30 | 22,33 | 18,84 | 13,41 | 8,05 |
| 40 | 16,75 | 13,93 | 9,63 | 5,54 |
| 50 | 13,40 | 11,02 | 7,45 | 4,14 |
| 60 | 11,17 | 9,10 | 6,04 | 3,27 |
| 70 | 9,57 | 7,74 | 5,06 | 2,68 |
| 80 | 8,38 | 6,73 | 4,34 | 2,25 |
| 90 | 7,44 | 5,94 | 3,79 | 1,93 |
| 100 | 6,70 | 5,32 | 3,36 | 1,68 |
| 120 | 5,58 | 4,39 | 2,72 | 1,33 |
| 150 | 4,47 | 3,48 | 2,11 | 0,99 |
| 170 | 3,94 | 3,05 | 1,82 | 0,84 |
| 200 | 3,35 | 2,57 | 1,51 | 0,68 |

## Heat stabilisation of polymers

### Example C1: without titanium dioxide powder (comparison example)

A two-component silicone rubber from Bayer, trade name Silopren® LSR 2040, is used as base component (addition crosslinking). After homogeneously mixing the two components with a dissolver the vulcanisation takes place at 180 °C for 10 minutes. Sample plates (ca. 10 x 15 cm) 6 mm thick are produced. The sample plates are heated at 80 °C in a furnace to constant weight (ca. 1 day). To check the thermal stability to heat a hot storage test is carried out. For this, a sample strip of size 5 x 7 cm is kept in a circulating air oven at 275 °C. The weight loss is measured.

### Example C2: Addition of titanium dioxide powder according to the prior art (comparison example)

A two-component silicone rubber from Bayer, trade name Silopren® LSR 2040, is used as base component (addition crosslinking). 1.5 wt.%, referred to the total batch, of titanium dioxide powder P 25 S (Degussa AG) is incorporated

5      for 5 minutes into one of the components, using a dissolver. Following this the vulcanisation and production of the sample plates take place as described in Example 1.

Sample strips of size 5 x 7 cm are stored at 275 °C. The weight loss is measured.

10     The Examples C3-5 are carried out similarly to C1, but using the titanium dioxide powders A1 according to the invention in C3, A3 in C4 and A7 in C5, instead of P25 S.

Table 4 shows the changes in length of the samples stored at 275°C after 1, 3 and 7 days.

15     The results demonstrate the effective heat protection stabilisation of polymers achieved by using the titanium dioxide powder according to the invention.

**Table 4: Two-component silicone rubber**

| Example | Length Change [%] after | | |
|---|---|---|---|
|  | 1 Day | 3 Days | 7 Days |
| C1 (comp.) | 98.6 | – | – |
| C2 (comp.) | 46.3 | 58.9 | 70.0 |
| C3 | 16.3 | 27.9 | 39.5 |
| C4 | 18.7 | 41.8 | 52.7 |
| C5 | 29.0 | 49.0 | 58.0 |

20

**Photocatalytic activity**

**Example D1: Titanium dioxide powder according to the prior art (comparison example)**

To determine the photocatalytic activity the sample to be
measured is suspended in 2-propanol and irradiated for one
hour with UV light.  The concentration of acetone formed is
then measured.

5  Ca. 250 mg (accuracy 0.1 mg) of titanium dioxide powder
P 25S (Degussa AG) are suspended using an Ultra-Turrax
stirrer in 350 ml (275.1 g) of 2-propanol.  This suspension
is conveyed by means of a pump through a cooler
thermostatically controlled to 24°C to a glass photoreactor
10  equipped with a radiation source and flushed beforehand
with oxygen.  An Hg medium-pressure immersion lamp of the
type TQ718 (Heraeus) with an output of 500 Watts serves for
example as radiation source.  A protective tube of
borosilicate glass restricts the emitted radiation to
15  wavelengths >300nm.  The radiation source is surrounded
externally by a cooling tube through which water flows.
Oxygen is metered into the reactor via a flow meter.  The
reaction is started when the radiation source is switched
on.  At the end of the reaction a small amount of the
20  suspension is immediately removed, filtered, and analysed
by gas chromatography.

A photoactivity k of $0.68 \times 10^{-3}$ mole $kg^{-1}min^{-1}$ is measured.
This is taken as base value 1.  The titanium dioxide powder
according to the invention has a somewhat lower
25  photocatalytic activity of 0.8 to 0.9.